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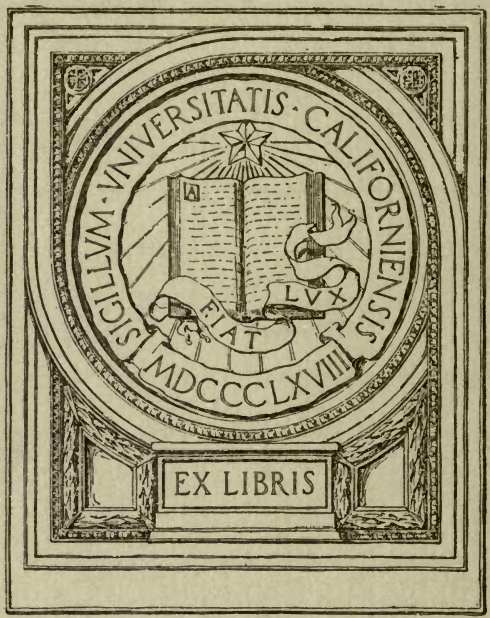

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The Solubility and Surface Energy of Fine Powders

A DISSERTATION

PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE GRADUATE SCHOOL OF THE OHIO STATE UNIVERSITY

UNIVERSITY OF CALIFORNIA

By

MERLE LEROY DUNDON

The Ohio State University
1922

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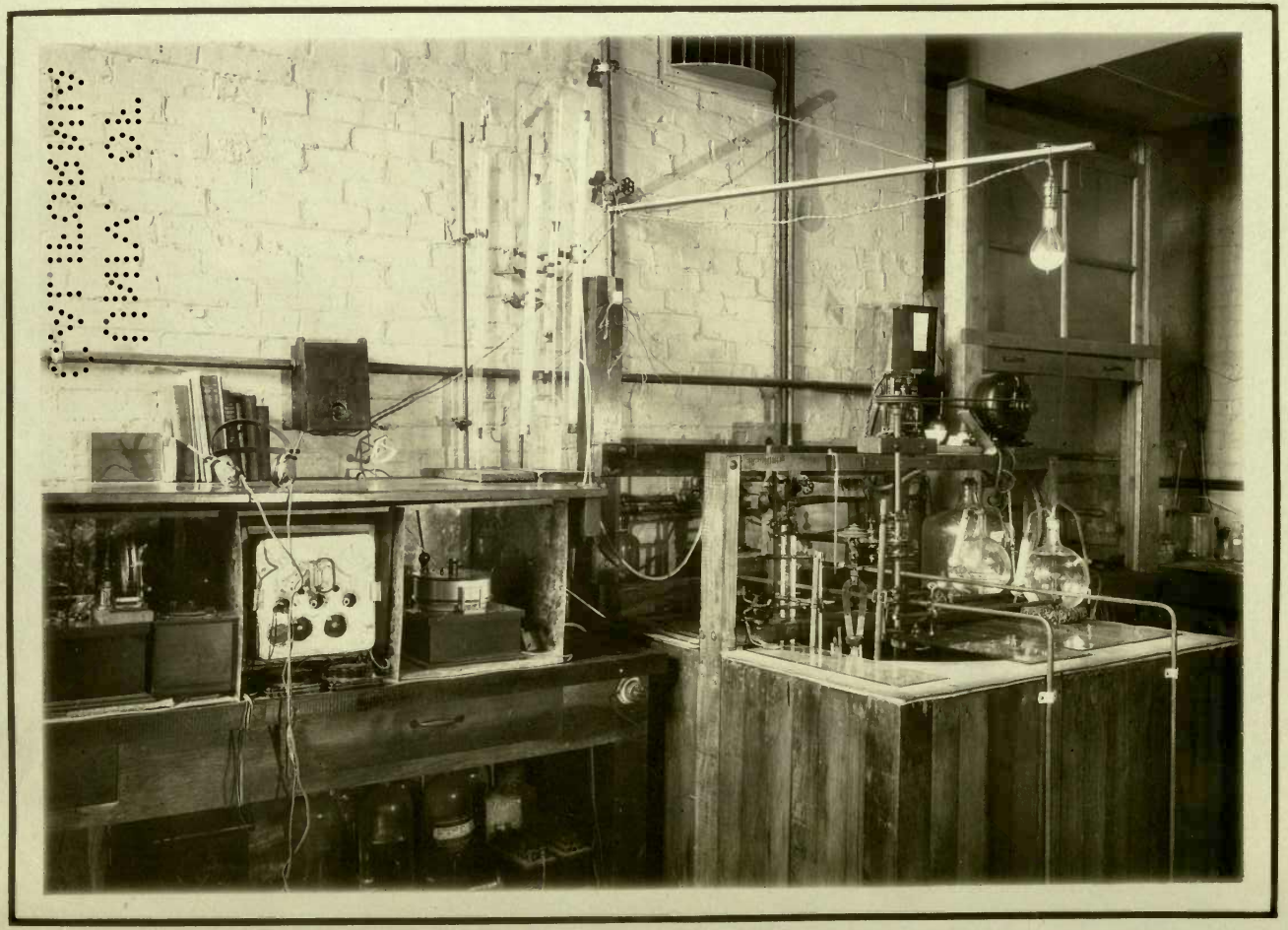

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The Solubility and Surface Energy of Fine Powders

Introduction

It is well known in a qualitative way that the solubility of very fine particles is greater than that of coarse ones. This is exemplified in the ordinary custom of digesting precipitates in order to facilitate their filtration. The importance of having available some quantitative knowledge of just how solubility depends on size is very apparent. Such data are needed in elucidation of the surface-energy relations of solids such as are now involved in the study of the colloidal state. In spite of its importance, however, the only available experimental data in this field are those of Hulett[1] for calcium and barium sulfates, and for mercuric oxide, and even these are admittedly qualitative.

In the present paper and the one which follows, we have repeated some of Hulett's work and have extended his general experimental method to several other substances in an effort to obtain reliable values for their surface energy.

[1] Hulett, *Z. physik. Chem.*, **37**, 385 (1901); **47**, 357 (1904). It is true that Marian Jones and J. R. Partington [*J. Chem. Soc.*, **107**, 1019 (1915)] measured the increased solubility of small calcium sulfate particles. Sauer [*Z. physik. Chem.*, **47**, 160 (1904)] also mentions incidentally the increased solubility of finely pulverized calomel in connection with the use of a calomel electrode. But it is not reported in either of these papers that the size of the particles was measured. It should be noted also that F. C. Thompson [*Trans. Faraday Soc.*, **17**, 391 (1922)] by quenching an iron-carbon alloy at 780°, then tempering part of it at 500° and another part at 650°, obtained cementite grains of different sizes. He determined the concentration of the carbon dissolved in the iron in the two cases by measuring the electrical resistance, and calculated an interfacial tension of 1350 dynes/cm.

Theoretical Part

Surface energy, σ, has been calculated by Hulett and by Freundlich, by substitution in the Ostwald-Freundlich equation,[2]

$$\frac{RT}{M} ln \frac{S_2}{S_1} = \frac{2\sigma}{\rho}\left(\frac{1}{r_2} - \frac{1}{r_1}\right) \quad (1)$$

where R is the gas constant, T the absolute temperature, M the molecular weight of the solid in solution, ρ the density of the solid, σ the surface energy per unit surface between the solid and its solution, and S_2 and S_1 are the solubilities of the particles of radii r_2 and r_1, respectively. In the derivation of this equation it is assumed that the particles are spherical,[3] that the dissolved solid obeys the gas laws, and that σ and ρ are independent of the size of the particles. Equation 1 does not hold for dissociated substances. Jones[4] takes into account the dissociation of the dissolved substance by combining Equation 1 with the equation of Storch,[5] which is

$$\frac{(1-\alpha)}{v} = K\left(\frac{\alpha}{v}\right)^m \quad (2)$$

where α is the degree of dissociation, v is the dilution and K and m are constants. When m is 2, Storch's equation becomes the familiar Ostwald dilution equation. The equation which Jones derived, by a combination of Equations 1 and 2 and by integrating between the limits α_1 and α_2, is

$$\frac{2\sigma}{\rho}\left(\frac{1}{r_2} - \frac{1}{r_1}\right) = \frac{RT}{M}\left[(n-1)(\alpha_1 - \alpha_2) - \frac{n}{m-1} ln \frac{1-\alpha_1}{1-\alpha_2} + \frac{m}{m-1} ln \frac{\alpha_1}{\alpha_2}\right] \quad (3)$$

where n is the number of ions formed from the dissociation of one molecule. While this equation is theoretically sound, its practical application is complicated by the fact that concentrations are expressed only in terms of dissociation and the constant m in Storch's equation. Inasmuch as small differences in dissociation correspond to rather large changes of concentration, small errors in expressing dissociations are quite serious.

In these fundamental derivations the ordinary expression for osmotic work done is $\frac{RT}{M} ln \frac{p_2}{p_1}$ *for one mole* of dissolved solute. Then, if a substance is dissociated and we assume that this dissociation is constant during the process, Equation 1 becomes

$$(1 - \alpha + n\alpha)\frac{RT}{M} ln \frac{S_2}{S_1} = \frac{2\sigma}{\rho}\left(\frac{1}{r_2} - \frac{1}{r_1}\right) \quad (4)$$

---

[2] First derived in its most general form by Willard Gibbs in 1876, "Scientific Papers," Longmans, Green and Co., 1906, N. Y., vol. I, p. 315. Freundlich, Kapillarchemie, Leipzig, 1920, p. 143.

[3] William Jacob Jones [*Ann. Physik*, **41**, 441 (1913)] has considered the influence of various geometrical forms instead of the spherical particles assumed in the general equation.

[4] W. J. Jones, *Z. physik. Chem.*, **82**, 448 (1913).

[5] Storch, *ibid.*, **19**, 13 (1896).

Values obtained by this simple equation approximate closely to those calculated by means of the rigorous equation of Jones, the differences being very small in comparison with the errors inherent in the data.

There is another point in this connection which is important. In substituting numerical values for the radii in the expression $\frac{2\sigma}{\rho}\left(\frac{1}{r_2}-\frac{1}{r_1}\right)$, r_2 is the radius of the smaller and more soluble particles, and is, of course, measured by microscopic observation; r_1 represents the radius of a large particle, in equilibrium with its own saturated solution. In Hulett's work (and also in the present work) this saturated solution containing the large particles was simply a saturated solution of the substance in equilibrium with *large crystals*. Since the crystal surfaces were flat, $1/r_1$ is $1/\infty$. It is true that Hulett's results seemed to show that particles 2μ in diameter were also in equilibrium with the saturated solution of the crystals. But one cannot be absolutely certain of the equilibrium, and if it is a question of choosing between $1/\infty$ and $1/2\mu$ there can be no doubt that it is preferable to write $1/\infty$ into the equation. In this case, Equation 4 assumes the form

$$(1-\alpha+n\alpha)\frac{RT}{M}ln\frac{Sr}{S}=\frac{2\sigma}{\rho r} \qquad (5)$$

and this is the equation which we have used throughout our work in calculating the surface energy.

In an interesting paper, Marian Jones and J. R. Partington[6] have attempted to test the validity of Equation 1 at 20°, 40° and 60°. Taking the known concentrations of saturated calcium sulfate solutions in equilibrium with gypsum crystals, they substitute these values for S_1 in Equation 1 and calculate S_2 for the respective temperatures and for various values of r_2, setting $r_1=\infty$, and making use of W. J. Jones' surface-energy value, 1050, calculated from Hulett's data. They have not measured the size of their particles, but have assumed a radius of 1μ, because their experimentally determined solubilities fit their calculated solubility curve for particles of this size. The surface-energy value, 1050, which takes into account the dissociation of the calcium sulfate, has unfortunately been substituted in Equation 1, which does not hold for dissociated substances. The result is that all of their calculated solubilities and radius values are much too high. This error is evident from the fact that their fine particles which give an increased concentration of 4.6% at 20° are considered to be of the same size as were found by Hulett to show no increased solubility, *although their own calculations are based on Hulett's data.*[7]

[6] Jones and Partington, *J. Chem. Soc.*, 107, 1019 (1915).

[7] It has seemed desirable to call attention to the difficulties with the conclusions reached by Jones and Partington, because the substance of their work has already been incorporated into two well-known chemical texts.

Apparatus

A thermostat was constructed which contained a regulator sensitive to a change of 0.0003° C. or less and which could be held constant within 0.001° for several hours. It consisted of a 400-liter copper kettle, well insulated and provided with a stirrer in the center. The toluene regulator, equipped with a Gouy[8] oscillating needle, was composed of a 30-meter coil of copper tubing 6 mm. in diameter which was connected to the glass top by a specially devised glass-metal joint.[9] Between the main tube and the glass top was inserted a coil of flexible hollow wire brass tubing. A tap and seal or "appendix" was attached to the highest point of the main tube by means of which toluene could be sucked through from the glass top, all air drawn out, and the mercury added without removing or inverting the glass bulb and top. The oscillating needle, which made one cycle every two seconds, was activated by an induction motor through a cam and worm gear. A 500-ohm relay with large graphite contacts was used.

The Wheatstone bridge arrangement for measuring conductivities was composed of a 100,000-ohm Curtis coil box, a Kohlrausch slide wire bridge with extension coils, a two-stage thermionic amplified with a Brandeis head set, and a good variable air condenser. An audio oscillator giving a frequency of 1000 was used as a source of current for measurements. The general arrangement was that advised by Washburn.[10] The telephone was connected to the bridge through the amplifier which was completely enclosed in a tin box. Each instrument rested on a paraffin cake and the whole system was surrounded by shielding of tin plate except in front. The bridge, the shielding and the bath were all grounded.

The conductivity water was made in a Bourdillon[11] type of still which furnished water having a conductivity of $0.4–1.0 \times 10^{-4}$ mhos.

The Kohlrausch type of conductivity cell with platinized electrodes that was used in this first work could be shaken violently by hand immediately upon addition of the powder. Other cells are described in the paper following.

Experimental Part

The method we have employed in measuring the increased solubility of small particles of calcium sulfate is essentially the same as that of Hulett. Into a saturated solution of calcium sulfate in equilibrium at 25° with large crystals, a quantity of the finely powdered calcium sulfate was introduced. The increase in concentration, and the return to the original concentration were noted by conductivity measurements. In order to calculate the concentration of a solution of a dissociated substance from

[8] Sligh, *J. Am. Chem. Soc.*, **42**, 60 (1920).
[9] Dundon, *ibid.*, **45**, 716 (1923).
[10] Washburn, *ibid.*, **35**, 177 (1913).
[11] Bourdillon, *J. Chem. Soc.*, **103**, 791 (1913).

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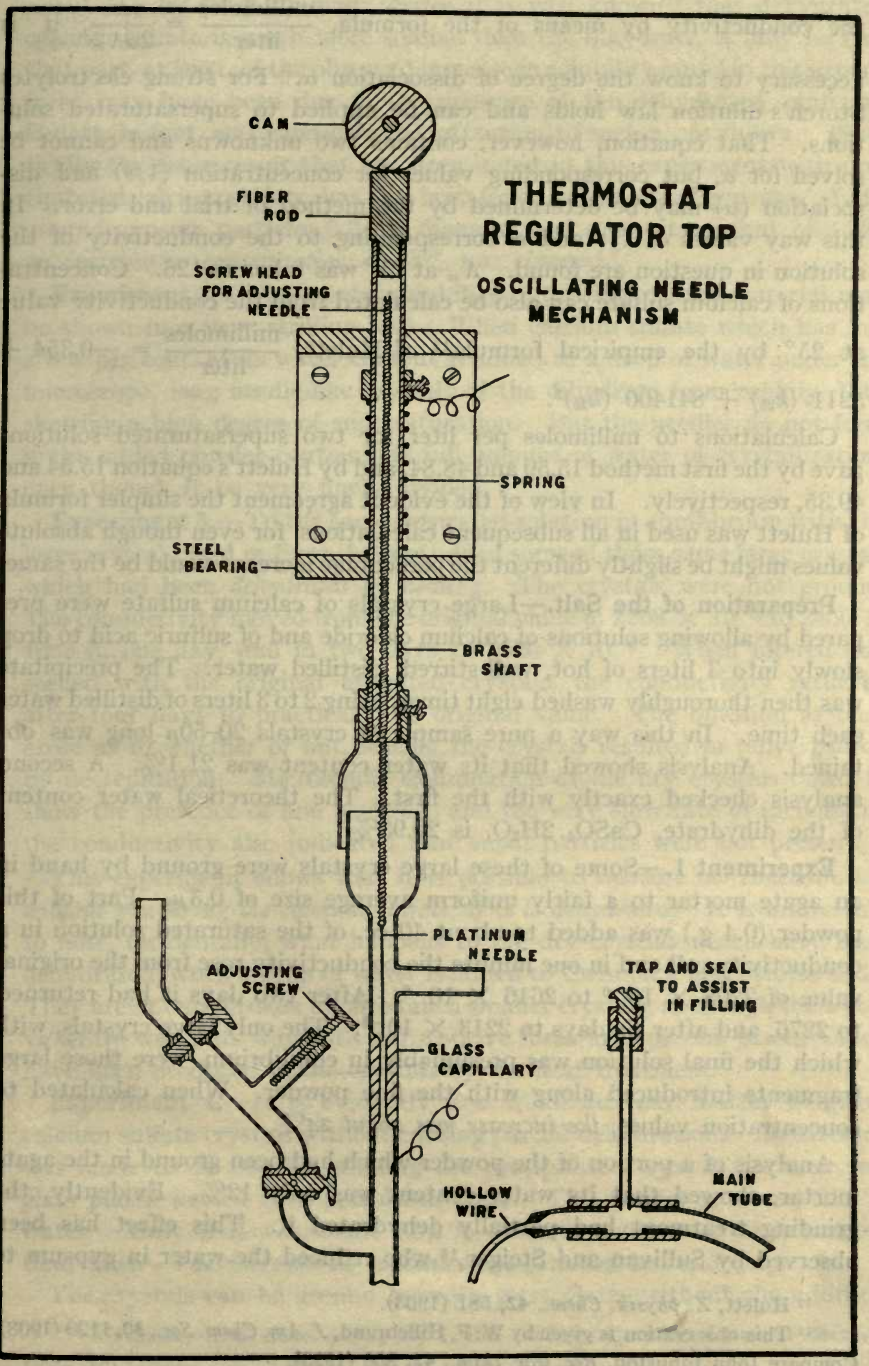

the conductivity by means of the formula, $\frac{\text{millimoles}}{\text{liter}} = \frac{k}{2\alpha\Lambda_\infty}$, it is necessary to know the degree of dissociation α. For strong electrolytes Storch's dilution law holds and can be applied to supersaturated solutions. That equation, however, contains two unknowns and cannot be solved for α, but corresponding values for concentration $(1/v)$ and dissociation (α) may be determined by the method of trial and error. In this way values of $1/v$ and α corresponding to the conductivity of the solution in question are found. Λ_∞ at 25° was taken as 126. Concentrations of calcium sulfate can also be calculated from the conductivity value at 25° by the empirical formula[12] of Hulett, $\frac{\text{millimoles}}{\text{liter}} = -0.354 + 5211\ (k_{25}) + 841400\ (k_{25})^2$.

Calculations to millimoles per liter for two supersaturated solutions gave by the first method 15.59 and 48.84, and by Hulett's equation 15.54 and 49.35, respectively. In view of the evident agreement the simpler formula of Hulett was used in all subsequent calculations, for even though absolute values might be slightly different the percentage increase would be the same.

Preparation of the Salt.—Large crystals of calcium sulfate were prepared by allowing solutions of calcium chloride and of sulfuric acid to drop slowly into 3 liters of hot, well-stirred, distilled water. The precipitate was then thoroughly washed eight times, using 2 to 3 liters of distilled water each time. In this way a pure sample of crystals 20–50μ long was obtained. Analysis showed that its water content was 21.1%. A second analysis checked exactly with the first. The theoretical water content of the dihydrate, $CaSO_4.2H_2O$, is 20.93%.

Experiment 1.—Some of these large crystals were ground by hand in an agate mortar to a fairly uniform average size of 0.3μ. Part of this powder (0.4 g.) was added to about 40 cc. of the saturated solution in a conductivity cell and in one minute the conductivity rose from the original value of 2208×10^{-6} to 2616×10^{-6}. After two days it had returned to 2276, and after six days to 2213×10^{-6}. The only large crystals, with which the final solution was presumably in equilibrium, were those large fragments introduced along with the fine powder. When calculated to concentration values, *the increase was about 24%.*

Analysis of a portion of the powder which had been ground in the agate mortar, showed that its water content was only 12%. Evidently, the grinding treatment had partially dehydrated it. This effect has been observed by Sullivan and Steiger,[13] who reduced the water in gypsum to

[12] Hulett, *Z. physik. Chem.*, **42**, 581 (1903).

[13] This observation is given by W. F. Hillebrand, *J. Am. Chem. Soc.*, **30**, 1120 (1908). Compare John Johnston, *Rec. trav. chim.*, **42**, 850 (1923).

about 5% by long grinding. Since it is well known[14] that dehydrated calcium sulfate is much more soluble than the dihydrate, it may be true that part, at least, of the observed increase in solubility noted in this experiment may have been due to the presence of the dehydrated material. Hulett, in fact, was careful to call attention to such a possibility. Practically the same result that has been noted in this experiment with precipitated calcium sulfate, has also been found with natural gypsum. With ground gypsum particles 0.3μ in diameter and a water content of 15%, *an increase in concentration of 28% was observed.*

Experiment 2.—The greater solubility of the dehydrated material may be shown in a very striking way. When calcium sulfate which has lost a few per cent. of its water content is added to a drop of water under the microscope, long needle-like crystals of the dihydrate form rapidly, thus showing a high degree of supersaturation. But the needles do not form if the added powder contains its full amount of water of crystallization, even though it be very finely divided.

Experiment 3.—To the same saturated solution in equilibrium with the large crystals used in Expt. 1, were added some of these same large crystals which had been *dehydrated by heating.* The crystals were not ground. The conductivity moved from the original value of 2208×10^{-6} to 2450×10^{-6} in one day, and in two days to 2520×10^{-6}. When filtered and seeded with the original hydrated crystals, the conductivity returned after four days to practically its original value. The question at once arose as to whether or not heating the crystals resulted in pulverization by decrepitation. Microscopic examination of the dry crystals failed to show the presence of fine particles, and the very slow rate of increase of the conductivity also indicated that small particles were not present.

This experiment shows that it is possible to *increase the concentration without powdering the calcium sulfate, if it is dehydrated.* It is interesting to note, incidentally, what happens to the dry crystals which have been dehydrated, when a drop of water is added to them on a microscopic slide. They are at once broken up into much smaller crystals, as though the water violently works its way with a disruptive force into porous places which have been produced in the crystals by the heat treatment.

Experiment 4.—It is evidently not at all an easy matter to grind calcium sulfate crystals without causing partial dehydration. An attempt was made to do this by grinding the precipitated crystals between two glass plates wetted with petroleum ether. The powder analyzed 21.1% water. Most of it was about 0.5μ in diameter, with very little smaller than that. *The increase in concentration obtained was 4.8%.*

The crystals can be ground between glass plates without the addition

[14] Marignac, *Ann. chim. phys.*, (5) I, 274 (1874). Cavazzi, *Industria chimica*, 1906, 366 (1906).

of petroleum ether and the powder will show by analysis its full water content, but it is difficult to obtain powder even as small as 0.5μ, because of the stickiness and the great resistance to rubbing.

Experiment 5.—In a further attempt to prevent dehydration on grinding, some clean natural gypsum crystals were ground in an agate mortar in a small room where the air was kept saturated by vapor from boiling water. The temperature was about 25°. Each lot of 0.1 g. powder was ground for 20 minutes. The powder so prepared showed a water content of 18.5%. It was then taken in small lots in the mortar, wet with conductivity water, ground until dry, and the resulting lumps were powdered. Analysis gave 21.0% water. Most of the particles were about 0.5μ in diameter, with a few 0.4μ. *An increase in concentration of 4% was found.*

Experiment 6.—It was observed, during examination of fine calcium sulfate particles under the microscope, that if water was used to wet the particles, a slight rubbing with the glass cover slip seemed to break them up into much smaller pieces. This suggested that the substance might be ground satisfactorily in the presence of water. Therefore, precipitated calcium sulfate crystals were wet with conductivity water and ground by hand in an agate mortar until dry. The resulting dry lumps were then ground until thoroughly powdered. The water content was 21.3%. The powder grains appeared very irregular in shape, and a large percentage of them were about 0.2μ, and some 0.3μ in diameter. *The increase in concentration, as shown by conductivity measurements, was 12.3%.*

Experiment 7.—Some of the ground powder used in Expt. 4, showing a water content of 21%, was heated at 100° for half an hour, until its water content had dropped to 15.5%. This powder when added to the saturated solution in the conductivity cell, *showed an increase of 257% in concentration.* There did not seem to be many smaller particles present after the heating than before, although, of course, there may have been a great deal of material too small to be visible in the microscope.

Discussion of Results

Examination of the results in Expts. 4, 5 and 6, shows that where precautions were taken to avoid dehydration, the increase in solubility due to the small size of the particles was not very great. In Expts. 4 and 5, where particles about 0.5μ in diameter were used, the average surface energy, calculated from Equation 5, taking i (that is, $1 - \alpha + n\alpha$) as 1.56, was 356 ergs per sq. cm. Calculation by Jones' Equation 3 gave 352 (a difference of about 1%), while an error of only 0.01μ in the diameter measurement would make a difference of 2% in the value for surface energy. In the microscopic estimation of the size of particles, the probable error is much greater than 0.01μ. It is more nearly 0.1μ. Thus it is clear that the simplified Equation 5 is amply sufficient for present needs. It

is also clear that very little reliance should be placed on our present knowledge of the surface energy of solids.

In Expt. 6, where the particles were estimated at 0.2μ in diameter, the calculated value of the surface energy was 385. The average for the two sizes, 0.5 and 0.2μ, is then about 370.

The question now arises as to why the above result differs from that of Hulett, who found a much larger increase in solubility. The possibility of slight dehydration is suggested by the fact that he does not specifically mention any moisture determination on his fine powder. Moreover, gypsum crystals are transparent, and have a low refractive index, and when finely powdered are difficult to observe sharply in the microscope, so that it is very uncertain how many particles too small to be visible might be present in the powder. When the material was wet almost until the last stage of grinding, as in our own Expts. 5 and 6, the probability of the occurrence of invisible small particles would be greatly lessened.

We wish to express our gratitude to the Grasselli Chemical Company for the fellowship grant under which this investigation was carried on.

Summary

1. A brief discussion is given of errors which appear in the literature in the calculation of surface energy and size of particles of calcium sulfate based on Hulett's data.

2. On the basis of the simplifying assumption that the degree of dissociation does not change with small changes of concentration, the van't Hoff factor, i, is introduced into the Ostwald-Freundlich equation, to replace the complicated correction formula of W. J. Jones.

3. Experimental data have been produced which show the great tendency of gypsum and precipitated calcium sulfate, $CaSO_4.2H_2O$, to become dehydrated during grinding, and the importance of this factor in relation to experiments on the solubility of finely powdered calcium sulfate.

4. Working with particles 0.2μ and 0.5μ in diameter a value of about 370 ergs/sq. cm. has been calculated for the surface energy of the dihydrate of calcium sulfate.

[The following paper is an account of work performed while the author was a National Research Council Fellow. This investigation was carried out after he had received the degree of Doctor of Philosophy from the Ohio State University and, with the consent of the Dean of the Graduate School, is bound here with the thesis.]

SURFACE ENERGY OF SEVERAL SALTS

Introduction.—In the preceding paper the method of calculating surface energy from the increased solubility of fine particles was considered, and a value for the surface energy of gypsum calculated from new data. In the present work an attempt has been made to measure the change in solubility due to change in size of particles for several other substances. The best opportunity for such an investigation occurs with substances of small solubility, in which case equilibrium comes about with such slowness that it can be followed by frequent conductivity measurements. Such solubility equilibria must, however, be easily obtained, and continued hydrolysis or other decomposition in solution must not occur. With many of the substances considered, such as lead sulfate, mercurous chloride and magnesium fluoride, some interfering factor of this sort soon developed, which made it impossible to obtain data of use in this study. Of those substances which gave positive results and which are mentioned in this paper, lead fluoride, because of its many favorable properties, was investigated most extensively.

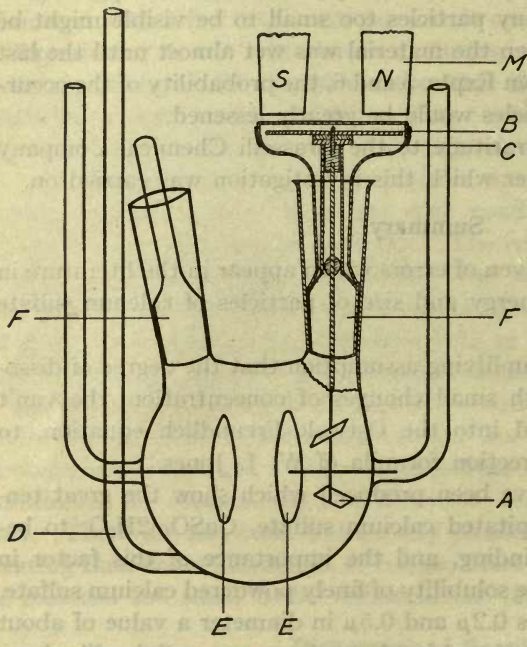

Fig. 1.—Conductivity cell

Experimental Method.—Fine powders have been obtained by hand-grinding in an agate mortar, with a mechanically operated mortar and pestle, or with a steel ball mill. Ordinarily, the powder was used directly, and the size of the smallest particles present in large numbers was the value recorded. Attempts were made to sort the particles into different sizes and to calculate the sizes by settling in water or alcohol, making use of Stokes' law. This method failed to yield satisfactory results because of the coalescence of the settling particles into clumps and also, no doubt, because of the adsorption effect at the surface of the small particles.[1] In the case of lead fluoride, how-

[1] Williams, *Trans. Faraday Soc.*, **18**, 53 (1922).

ever, an air elutriation method was devised, of such a sort that the powder was carried upward through a long glass tower, and very uniformly sized particles, 0.3μ, were obtained, with no particles larger than 0.5μ. Consequently, a good deal of confidence may be placed in the results for lead fluoride.

Measurement of the size of particles was made with a calibrated scale in the eyepiece of a microscope having a magnification of 1800 diameters. Several conductivity cells were used, including the Kohlrausch type, some large flasks with suspended electrodes, and one cell especially designed for this work. This cell is shown in Fig. 1. The platinum paddle-wheel stirrer A can be operated by a magnet M outside the cell. The stirrer shaft of platinum was set into a brass plug at the top and had a drop of glass fused around it lower down to keep it in position. The steel bar B was fastened to the brass plug with a small screw which passed through the washers C. All metal parts other than the platinum were gold-plated. The glass cap above the bar is held in position by a rubber band. F is the ground-glass stopper.

The data for calculating concentrations from conductivity values, such as temperature coefficients, equivalent conductivities, etc., have been obtained in most cases from the work of Kohlrausch. A water correction has been applied to all conductivity values given.

Lead Fluoride

No crystallographic data concerning lead fluoride could be found in the literature and no crystals larger than a few microns were made. However, it was determined[2] that they belong to the orthorhombic system and have an average refractive index of 1.83 and a hardness of about 2.

Hydrolysis of the Solution.—Saturated lead fluoride solutions are distinctly acid, having a Sörensen value of about 1, and the acidity changes very little over a considerable range of dilution. Kohlrausch[3] found that in the variation of equivalent conductivity with dilution at 18° hydrolysis was not indicated, and his results on this point have been widely quoted. It was found in this investigation at 25° that, although a given solution remained constant, considerable hydrolysis took place on dilution, giving a value for the equivalent conductivity at infinite dilution which is much too high.

Calculation of Concentrations.—A carefully prepared saturated solution had a conductivity of 513×10^{-6} mhos, and gravimetric analysis showed the equivalent concentration to be 0.00555. Experimental data were then obtained from which a curve of equivalent conductivity against the cube root of the concentration was plotted. From this a second curve was plotted giving equivalent concentrations directly in terms of specific conductivity. Several gravimetric analyses of supersaturated solution prepared from fine powder checked this curve almost exactly.

Method of Obtaining Equilibrium.—A saturated solution was pipetted into the cell from a stock solution, powder added and the cell shaken

[2] Thanks are due to Professor W. J. McCaughey of the Department of Mineralogy, Ohio State University, for assistance in making these determinations.

[3] Kohlrausch, *Z. physik. Chem.*, **64**, 134 (1908).

thoroughly, after which the maximum conductivity was reached in from two to ten minutes. The conductivity then gradually decreased for several days. Sometimes, in order to hasten the final equilibrium, the solution was carefully filtered and coarse crystals were added. In some cases also, a few drops of conductivity water were added to the supersaturated solution in order to hasten the final equilibrium. When too much water was added the conductivity again increased to approach the normal equilibrium. This change served as a means of determining whether a solution of conductivity higher than normal at the end of a test was still supersaturated, or whether the higher conductivity was due to impurities.

TABLE I

SOLUBILITY VALUES FOR LEAD FLUORIDE

At 25°. Size of particles 0.3μ except in No. 7 where it was about 0.2μ

	Conductivity × 10^6[a]			High cond. corr. for return	High concn.	High concn. corr. for return[b]	Concn. from grav. analysis	% Increase		Wt. in g. added to 50 cc.
	Begin.	High	End		×10^3	×10^3	×10^3	Uncorr.	Corr.	
1	513	547	523	536	6.02	5.88	..	8.5	6	0.06
2	513	555	524	544	6.14	5.99	..	10.6	8	0.05
3	513	549	515	548	6.07	6.03	..	9.4	8.7	0.1
4	513	547	...	...	6.03	..	5.99	8.7	..	...
5	513	545	...	...	6.00	..	6.00	8.1	..	...
6	(H_2O)	541	516	538	5.93	5.90	..	6.9	6.3	0.3
7	582	590[c]	538	565	..	6.28	..	..	13.1	0.025
8	543	557[c]	521	549	..	6.06	..	..	9.2	0.13
					(less than)			(less than)		
9	598	581[c]	543	550	6.32	6.07	..	13.8	9.4	0.3

[a] A water correction not greater than 2 × 10^{-6} was applied to the saturated solutions to bring them to the value determined gravimetrically as correct (0.00555 gram-equivalents per liter).

[b] When the supersaturated solution in contact with crystals failed to return to the conductivity value corresponding to a normal saturated solution, the presence of impurities was indicated. On this assumption, therefore, in columns marked "Corr. for return" a correction equal to the difference between the beginning and end solutions has been subtracted from the high value.

[c] Five minutes after adding powder.

In Table I are tabulated the most reliable data obtained on the increase in solubility of lead fluoride. In the first three experiments, the fine powder was added to the saturated solution and the solution kept until the conductivity had again decreased to a point where it was constant. In Expts. 4 and 5 the solution was filtered as soon as possible after the addition of the fine powder and the concentration also determined by gravimetric analysis. In No. 6 the powder was added directly to water and the solution observed until it had returned nearly to the saturated value. In Expt. 7 a supersaturated solution was prepared by heating a solution to boiling with an excess of crystals and filtering the liquid into the cell. Fine

powder was then added and the conductivity found to increase slightly and then decrease to a value considerably below the starting point. This showed that the solution was not sufficiently concentrated to be in equilibrium with the finest particles present. The final conductivity when the solution became constant indicates considerable contamination, due either to increased hydrolysis at the higher temperature or to impurities acquired during the boiling and filtering. The increase calculated after applying corrections is high, but the powder was an unusually fine sample.

No. 8 is very similar to No. 7, except that the original solution was less concentrated and the maximum concentration reached was lower. In the case of No. 9, the original solution was more concentrated than a solution in equilibrium with the powder. This, therefore, sets an upper limit on the maximum increase in solubility for a powder of the size used. In a similar experiment not tabulated, an increased concentration of 20% was found to be much too high and a very rapid decrease occurred upon addition of the powder. It is interesting to note that the concentration reached five minutes after addition of the powder is approximately the same in No. 8 as in No. 9 although the point was approached from different directions.

Nine per cent. has been taken as the value representing the increased solubility of lead fluoride powder 0.3μ in diameter. Working with a saturated solution of lead fluoride in 95% alcohol, an effect of about the same magnitude was found.

Lead Iodide

Lead iodide gave a very small increased solubility effect. It is soft and flaky and is difficult to grind into a fine powder, even with the aid of fine quartz. The smallest particles were about 0.4μ in diameter. In two minutes an increase in concentration of about 2% was obtained.

Strontium Sulfate

Small particles added to solutions of strontium sulfate failed to disappear and allow the solution to return to the normal equilibrium. This may be due partially to a very slow rate of solution in this case, but similar difficulties occurred and are discussed in greater detail in connection with barium sulfate. While an initial increase as high as 25% was obtained for particles 0.3μ in diameter, there was never more than a 2% return from the maximum.

Silver Chromate

A precipitate composed of good orthorhombic crystals from 10 to 50μ in length was made by mixing very dilute hot solutions of silver nitrate and potassium chromate. The crystals were easily ground. The average size of the small particles was considered to be 0.3μ. The solutions were constant in cells with bare electrodes, but the conductivity of a saturated solution decreased when put into a cell with platinized electrodes. After

adding 0.35 g. of powder to 500 cc. of solution and stirring the mixture with pure air, 24 hours was required to reach a maximum conductivity. The resulting solution when pipetted into another cell and stirred in contact with coarse crystals by means of a platinum paddle-wheel stirrer showed a decrease in conductivity for three days. After this time a slight but gradual increase set in, probably due to contamination of some kind. Two experiments at 26° agreed very closely, the fine powder causing an increase in equivalent concentration from 0.192×10^{-6} to 0.218×10^{-6}, or 13.5%, and the return in three days was 7%. In view of possible contamination or decomposition affecting the conductivity, 10% seems to be the most reasonable estimate of the real increase.

Calcium Fluoride

In one experiment pure mineral fluor spar was used. For the others, C. P. calcium fluoride was ground fine and digested several times with water until only coarse crystals remained. In some cases the powder was all added at once, and in other cases at intervals until no more effect was noticed on further addition. The time required for the powder to produce a maximum conductivity was usually from three to five minutes, but in one case was 24 minutes. This was followed by a decrease for about five days with all the solid added still present. With four experiments the increases were 24%, 19%, 32% and 29%, and the subsequent decreases were 10.5%, 15%, 12% and 17%. Considering the possible influence of impurities on the conductivity and the slow digestion back to the normal value the real increase in concentration for a given powder cannot be more than the original increase nor less than the return. Therefore, 18% is taken as the value for use in calculating the surface energy. The size of the finest powder was 0.2μ–0.3μ with some larger particles.

Barium Sulfate

The method used for strontium sulfate was not successful with barium sulfate, because of the failure of the fine particles in the solution to disappear or grow to a larger size in any reasonable length of time.

Instead, a highly supersaturated solution (at 30°) in which the barium sulfate did not precipitate was prepared by mixing approximately equivalent quantities of very dilute sulfuric acid and barium hydroxide. The conductivity of this solution was constant at 21.4×10^{-6}. Fine barium sulfate, 0.2μ in size, was added, whereupon the conductivity fell in five hours to 16×10^{-6} where it remained practically constant for three days. Some of the clear solution was then pipetted into another cell and large crystals, 2μ–20μ, were added. The change was slow, but in three days the conductivity fell to 12.9×10^{-6}. If it is assumed that the correction for water and impurities, such as excess acid or base, is 9.3×10^{-6} (the difference between the last value and the normal value for a saturated solution),

the solubility of particles 0.2 μ in diameter is 90% greater than that of the larger crystals.

Failure of Particles to Disappear or Grow

Attention has just been called to the failure of small barium sulfate particles to dissolve. This was also true of all the other substances studied, although to a more limited extent. Whenever, upon addition of a finely powdered substance to its saturated solution, the conductivity had gone up and then had slowly returned to its initial normal value, the expectation was that *all* of the smaller particles had dissolved and crystallized from the supersaturated solution onto the large crystals present. But this is not what happened. Particles were left in the solution at the end, which were just as small apparently as those present at the beginning, and these small particles, even though in intimate contact with large crystals, showed no tendency to dissolve. Frequently, large crystals formed in solution without seeding, starting with small uniform particles, as in the case of lead fluoride; but here, too, at the end of the process many small ones remained.

These facts indicate either that a large part of the increased solubility is due to particles in the powder too small to be seen and measured, or soon after entering the solution the increased solubility of the small particles is decreased by some adsorption effect such as the acquisition of a charge. The latter explanation seems more in harmony with the facts.

This effect was shown in a striking manner by the behavior of barium sulfate particles. Several very fine precipitates were made from barium hydroxide and sulfuric acid. One sample was made 0.1 *N* acid, one alkaline to the same degree, and the others were neutral. The precipitates were not retained by a filter, did not settle for several hours, and under the microscope most of the particles appeared to be 0.2μ–0.3μ or less in size. After standing for three months and being frequently shaken, they could be filtered, but under the microscope most particles still appeared to be as small as 0.3μ and certainly few, if any, were larger than 0.5μ. One of the samples was then boiled under a reflux condenser for a week with no visible change even when seeded with large crystals. The particles were found to have a negative charge as they migrated very definitely in a U-tube under a potential of 125 volts.

When 10 cc. of concd. hydrochloric acid was added to 100 cc. of the suspension and the boiling continued, a marked change took place. After a few hours particles several microns in length appeared, and after four days all particles were at least 1.5μ and some were as large as 3μ $\times$ 10μ.

If the growth of large particles at the expense of the smaller ones is a surface-energy effect, then the hydrochloric acid must act either to increase the surface energy at the solid-liquid interface, or else to remove those

interfering factors which previously had prevented the normal surface energy from exerting its influence.

If we consider only the Ostwald-Freundlich equation, the calculated increase in solubility as particles become very small is so large that it seems improbable, and we are led to believe that some other factor enters to prevent actual attainment of the solubility predicted. W. C. M. Lewis[4] has proposed an expression, also independently developed and extended by Knapp,[5] which is based on the assumption that an electrical charge present on the surface of a small particle would decrease the solubility of such a particle. The curve plotted by Knapp from his equation shows that after a certain decrease in size a maximum solubility is reached, and for smaller particles the solubility is again diminished as we pass into the region of colloids. It seems probable that such a charge, by decreasing the surface energy and thus diminishing the increased solubility, may bring about a condition of equilibrium and prevent the further growth of particles at any size between those of a stable colloid and coarse crystals. If this is true, then the increased solubility for a definite size of particle would depend largely on conditions in the solution, and surface-energy calculations based on a solubility increase may be in error from this cause.

Calculation of Surface Energy.—By substituting the data giving the solubility of different sized particles in the equation[6]

$$\sigma = \frac{i\,RTr\,\rho\,ln\,\frac{Sr}{S}}{2M} \qquad (1)$$

it is possible to calculate the surface energy at the solid-liquid interface. It is evident, however, that all data obtained so far, including those of the

TABLE II

CALCULATED VALUES FOR SURFACE ENERGY

Substance	Mol. wt.	Density	Mol. vol.	Diam. of particles μ	% Sol. increase	Temp. °C.	i	σ	Hardness
PbI_2.....	461.04	6.16	74.8	0.4	2	30	1.97	130	very soft
$CaSO_4.2H_2O$[a].	172.16	2.32	74.2	0.2–0.5	4.4–12	30	1.56	370	1.6–2
Ag_2CrO_4.....	331.76	5.52	60.1	0.3	10	26	1.95	575	about 2
PbF_2.....	245.20	8.24	29.7	0.3	9	25	1.70	900	about 2
$SrSO_4$.....	183.69	3.96	46.4	0.25	26	30	1.82	1400	3.0–3.5
$BaSO_4$[b].....	233.43	4.5	52	0.1 (Hulett)	80	25	1.96	1250	2.5–3.5
	233.43	4.5	52	0.2	90	30	1.96	3000	2.5–3.5
CaF_2.....	78.07	3.18	24.6	0.3	18	30	1.97	2500	4

[a] See previous paper for discussion.

[b] The reason for the large difference in the two values of σ lies in the difference in the estimated size of the particles.

[4] Lewis, *Kolloid Z.*, **5**, 71 (1909).

[5] Knapp, *Trans. Faraday Soc.*, **17**, 457 (1922).

[6] For a discussion of this equation see the previous paper. It is equation (5) transposed.

present paper, are liable to so many errors that such calculations cannot be made with any great degree of exactness. In fact, besides the charge effect, the unknown shape of the fine particles, the errors in measurement of their size, the different rate of solution of different crystal faces, and the influence of crystal habit on the immediate growth of the particles, are certainly factors which interfere very seriously with the applicability of an equation based on the assumption that particles are spherical with uniform surfaces. However, the values for surface energy in Table II are the most nearly correct that can be obtained from data available at this time.

It will be seen that there is a rough proportionality between surface energy and hardness, as might be expected. It is further evident from Equation 1 that, other things being equal, the surface energy should vary directly as the density and inversely as the molecular weight; in other words, the surface energy should vary inversely as the molecular volume. This general relation is indicated by the table. However, the solubility increase varies greatly with different substances, and it is evident that such a relation can hold only for substances of the same general type.

This inverse relation between surface energy and molecular volume is approximately true for the fused lithium, sodium, potassium, rubidium and cesium compounds of fluorine, chlorine, bromine and iodine, and their nitrates and sulfates. Of all these alkali salts[7] lithium fluoride has the smallest molecular volume and consequently the largest surface energy. At 1270° it is 201 ergs per sq. cm., at 1000° it is 237, and at 870° it is 250, making an extrapolated value of about 350 at 25°, for the supercooled liquid. By substituting 350 for σ in Equation 1 the calculated increase in solubility for particles of lithium fluoride 0.3μ in diameter would only be about 1%. As a matter of fact, it was not possible with the methods employed in this investigation to detect an effect with lithium fluoride as great as 0.5%, showing the very slightly increased solubility of fine powders with substances of small molecular weight.

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Summary

1. A value for the surface energy has been calculated from the increased solubility of small particles for lead fluoride, lead iodide, silver chromate, strontium sulfate, barium sulfate and calcium fluoride.

2. It has been shown that a rough proportionality exists between surface energy and hardness, and the inverse proportion between surface energy and molecular volume, predicted by the Ostwald-Freundlich equation, has been indicated.

[7] F. M. Jaeger, *Verslag Akad. Wetenschappen Amsterdam*, **17**, 555 (1914); *Z. anorg. allgem. Chem.*, **101**, 1 (1917).

3. It has been observed that fine particles may have their solubility diminished by an electrical charge or adsorption effect on the surface.

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AUTOBIOGRAPHY

I, Merle Leroy Dundon, was born in Edingburgh, Ohio, October 27, 1892. My secondary education was received in the public and high schools of Rootstown and Ravenna, Ohio, and my undergraduate education at Mount Union College from which I received the Degree of Bachelor of Science in 1917. Following this I began my graduate work at the Ohio State University. During the war I entered the service in the infantry and was later transferred to the Chemical Warfare Service and located at the American University Experiment Station. Upon being discharged, I returned to the Ohio State University, where I was an assistant in the department of General Chemistry from 1919 to 1921, and was Grasselli Fellow during the year 1921–1922. In 1920, I received the Degree of Master of Science, and in 1922 the Degree of Doctor of Philosophy. The following year, working under a National Research Council Fellowship, I continued the investigation on the same subject as that of my Doctor's Dissertation.

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